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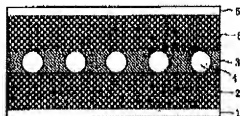
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(54) SECONDARY BATTERY AND ITS MANUFACTURE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a secondary battery that can precisely control the distance between both electrodes without using a separator which does not contribute to ion conductivity, as is conventionally done, obviates the need of the consideration on liquid leakage, and can provide battery performance equivalent to a lithium ion second battery using a conventional liquid electrolyte.

SOLUTION: This secondary battery has a structure provided with: a positive electrode composed by forming a positive electrode active material layer 2 on a positive electrode collector 1; a negative electrode composed by forming a negative electrode active material layer 6 on a negative electrode collector 5; and an ion conductive layer 3 formed from a nonfluidic ion conductive composition containing spacer particles 4, between the positive electrode active material layer 2 and the negative electrode active material layer 6, to control the distance between the positive electrode active material layer 2 and the negative electrode active material layer 6.



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CLAIMS

[Claim(s)]

[Claim 1]A rechargeable battery comprising:

An anode which formed a positive active material layer in a positive pole collector.

A negative electrode which formed a negative electrode active material layer in a negative pole collector.

An ionic conduction layer which consists of an ion-conductive constituent of non fluidity containing a spacer particle which controls distance of this positive active material layer and negative electrode active material layer between the above-mentioned positive active material layer and a negative electrode active material layer.

[Claim 2]The rechargeable battery according to claim 1, wherein mean particle diameter of a spacer particle is 5 micrometers - 50 micrometers.

[Claim 3]The rechargeable battery according to claim 1, wherein particle size distribution of a spacer particle is the distribution by which not less than 80% of all the particles are contained in the 0.3 time thru/or twice as many range of mean particle diameter as this.

[Claim 4]The rechargeable battery according to claim 1, wherein shape of a spacer particle is spherical.

[Claim 5]A manufacturing method of a rechargeable battery characterized by comprising the following.

A process of producing an anode and a negative electrode which formed a porous active material layer in a charge collector.

A process which apply to one of the active material layer surfaces mixed liquor of the above-mentioned anode and a negative electrode which mixed a monomer and a spacer particle to an electrolysis solution, and the active material layer surface of the above-mentioned anode and a negative electrode is made to counter them, and is laid on top of them at least.

A process of polymerizing a monomer in the state where it piled up.

[Claim 6]A manufacturing method of the rechargeable battery according to claim 5, wherein mean

particle diameter of a spacer particle is 5 micrometers - 50 micrometers.

[Claim 7]A manufacturing method of the rechargeable battery according to claim 5, wherein particle size distribution of a spacer particle is the distribution in which not less than 80% of all the particles are contained in the 0.3 time thru/or twice as many range of mean particle diameter as this.

[Claim 8]A manufacturing method of the rechargeable battery according to claim 5, wherein particle size distribution of a spacer particle is the distribution in which not less than 80% of all the particles are contained in the 0.3 time thru/or twice as many range of mean particle diameter as this.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to a rechargeable battery and a manufacturing method for the same. It is related with the ionic conduction layer of a rechargeable battery in more detail.

[0002]

[Description of the Prior Art]The request to the small size and the weight saving of a portable electronic apparatus is dramatically large. It depends for the realization on the improved efficiency of a cell greatly, and development of various cells and improvement have been advanced that it should correspond to this. The characteristic required of a cell has high tension, high energy density, safety, the optionality of shape, etc. A rechargeable lithium-ion battery is a rechargeable battery with which it is expected that high tension and high energy density will be most realized also in an old cell.

The Improvement is advanced briskly even now.

[0003]A rechargeable lithium-ion battery has an ionic conduction layer inserted into an anode and a negative electrode, and this anode and negative electrode as that main component. In the rechargeable lithium-ion battery with which the present practical use is presented, to an anode. What applied to the charge collector the positive active material which consists of powder, such as a lithium cobalt multiple oxide, and was made tabular is used, and what applied to the charge collector the negative electrode active material which consists of powder of a carbon system material, and was made tabular is used for the negative electrode. What filled the electrolysis solution of the non-drainage system on porosity films, such as polypropylene, is used for the ionic conduction layer.

[0004]It is required that an ionic conduction layer should require that there should be no electron conductivity, and battery capacity top ion conduction resistance should be low. That is, if resistance of an ionic conduction layer is made low, the charge and discharge in a high current will become more possible. On the other hand, it is required that two electrodes should be separated in

a predetermined distance via an ionic conduction layer so that between two electrodes (an anode and a negative electrode) may not connect too hastily. It becomes an important point to separate two electrodes in a predetermined distance from a viewpoint of obtaining the battery capacity where the short circuit was prevented and stabilized.

[0005]As mentioned above, using the separator which consists of a porosity film, the rechargeable lithium-ion battery with which the present practical use is presented separates two electrodes with this separator, and enables movement of the ion between two electrodes by being filled up with the electrolysis solution which bears ion conduction between two electrodes further. In order to maintain the electric interengagement of two electrodes and a separator, the structure which becomes firm armor cans, such as metal, from the separator inserted between two electrodes and these two electrodes is stored, and it is made the structure which puts a pressure on this structure from the exterior. The art about a rechargeable lithium-ion battery with such a structure is indicated by JP,H8-83608,A, for example.

[0006]Since the rechargeable lithium-ion battery constituted as mentioned above has included the electrolysis solution, the consideration to the leakage of an electrolysis solution is needed. Then, it inquires briskly as a theme with important carrying out immobilizing of the ionic conduction layer.

[0007]As art about the ion-conductive constituent of non fluidity, polymers, such as polyethylene oxide, have a polymer solid electrolyte which dissolved the salt. However, since this polymer solid electrolyte has strong ion conduction resistance at ordinary temperature at present, it is difficult to apply to a practical rechargeable lithium-ion battery.

[0008]There is a gel electrolyte which gelled the electrolysis solution used with a common rechargeable lithium-ion battery as immobilizing art in which low ion conduction resistance is realizable by polymer. The art about the cell which used the separator and the gel electrolyte together is indicated by the U.S. Pat. No. 5,609,974 item. The art about a gel electrolyte battery in which the gel electrolyte of porous state was used like a separator is indicated by the U.S. Pat. No. 5,460,904 item. In this case, although a separator like a porosity film is not used, the gel film of a polyvinylidene fluoride system which held the electrolysis solution by porous state has structure which separates between two electrodes.

[0009]

[Problem(s) to be Solved by the Invention]However, although between two electrodes is separated by using the gel electrolyte of porous state like a separator in the art indicated by the above-mentioned U.S. Pat. No. 5,460,904 item, When many electrolytes are made to contain by the inside of gel for the improvement in battery capacity, there is a problem that control of the distance between two electrodes is difficult, and the stable battery capacity is not obtained.

[0010]Since the separator used as the hindrance of ion conduction is contained as a component in the invention indicated by the above-mentioned U.S. Pat. No. 5,609,974 item, ion conduction resistance is strong. Thus, there is a problem that the performance which is equal to the cell using a liquid electrolyte, i.e., battery capacity called the charge and discharge by a high current, is not expectable even if it replaces an electrolysis solution with a gel electrolyte with the structure of having the conventional separator using an electrolysis solution.

[0011]In the art currently indicated by the above-mentioned U.S. Pat. No. 5,460,904 item. Although the separator which does not contribute to ion conduction which is used for the conventional cell is not used, since the electrolysis solution which is not gelled inside the inside of an active material layer or ionic conduction layer of an electrode exists, the problem that the consideration to the leakage of an electrolysis solution is needed is left behind.

[0012]This invention solves the above problems and the separator which does not contribute to ion conduction which is used from the former can control the distance between two electrodes precisely, without using it. It aims at providing the rechargeable battery with which the battery capacity which is equal to the rechargeable lithium-ion battery which did not need the consideration to liquid leakage and uses the conventional liquid electrolyte is obtained.

[0013]

[Means for Solving the Problem]The 1st rechargeable battery of this invention is characterized by comprising:

An anode which formed a positive active material layer in a positive pole collector.

A negative electrode which formed a negative electrode active material layer in a negative pole collector.

An ionic conduction layer which consists of an ion-conductive constituent of non fluidity containing a spacer particle which controls distance of this positive active material layer and negative electrode active material layer between the above-mentioned positive active material layer and a negative electrode active material layer.

[0014]In the 1st rechargeable battery of the above, mean particle diameter of a spacer particle of the 2nd rechargeable battery concerning this invention is 5 micrometers - 50 micrometers.

[0015]In the 1st rechargeable battery of the above, particle size distribution of a spacer particle of the 3rd rechargeable battery concerning this invention is the distribution by which not less than 80% of all the particles are contained in the 0.3 time thru/or twice as many range of mean particle diameter as this.

[0016]The 4th rechargeable battery concerning this invention has spherical shape of a spacer particle in the 1st rechargeable battery of the above.

[0017]A manufacturing method of the 1st rechargeable battery of this invention is characterized by comprising:

A process of producing an anode and a negative electrode which formed a porous active material layer in a charge collector.

A process which apply to one of the active material layer surfaces mixed liquor of the above-mentioned anode and a negative electrode which mixed a monomer and a spacer particle to an electrolysis solution, and the active material layer surface of the above-mentioned anode and a negative electrode is made to counter them, and is laid on top of them at least.

A process of polymerizing a monomer in the state where it piled up.

[0018]In a manufacturing method of the 1st rechargeable battery of the above, mean particle

diameter of a spacer particle of a manufacturing method of the 2nd rechargeable battery concerning this invention is 5 micrometers - 50 micrometers.

[0019]In a manufacturing method of the 1st rechargeable battery of the above, particle size distribution of a spacer particle of a manufacturing method of the 3rd rechargeable battery concerning this invention is the distribution by which not less than 80% of all the particles are contained in the 0.3 time thru/or twice as many range of mean particle diameter as this.

[0020]In a manufacturing method of the 1st rechargeable battery of the above, particle size distribution of a spacer particle of a manufacturing method of the 4th rechargeable battery concerning this invention is the distribution by which not less than 80% of all the particles are contained in the 0.3 time thru/or twice as many range of mean particle diameter as this.

[0021]

[Embodiment of the Invention]This invention persons use the ion-conductive constituent of non fluidity, such as a gel electrolyte, for an ionic conduction layer, The separator which does not contribute to ion conduction which is used from the former can control the distance between two electrodes precisely, without using it, The result of having repeated research to the purpose of obtaining the rechargeable battery with which the battery capacity which is equal to the rechargeable lithium-ion battery which did not need the consideration to liquid leakage and uses the conventional liquid electrolyte is obtained, By composition in which the particles which have the suitable shape which controls the distance between two electrodes, and a size in the ionic conduction layer which consists of an ion-conductive constituent of non fluidity are made to mix, it finds out that said purpose can be attained, and came to complete this invention.

[0022]Drawing 1 is a principal part cross section showing the 1 embodiment of the rechargeable battery obtained by this invention, and shows the single electrode layered product. The positive active material layer where 1 was formed in the positive pole collector and 2 was formed on the positive pole collector 1 in the figure, The ionic conduction layer which consists of non fluidity constituents, such as a negative electrode active material layer where 5 was formed in the negative pole collector and 6 was formed on the negative pole collector 5, and a gel electrolyte in which 3 has been arranged between the positive active material layer 2 and the negative electrode active material layer 6, 4 is a spacer particle which is mixed into the ionic conduction layer 3 and controls the distance between the positive active material layer 2 and the negative electrode active material layer 6, i.e., inter electrode distance.

[0023]If it is metal stable within a cell as the positive pole collector 1 and the negative pole collector 5 which are used for the anode and negative electrode concerning this invention, it is usable, but copper is preferably used as aluminum and the negative pole collector 5 as the positive pole collector 1. Although it is usable in anythings, such as foil, reticulated, and EKUSU pan Doume Tal, the shape of the charge collectors 1 and 5 is preferably used, in order that what has the large surface area of reticulated, EKUSU pan Doume Tal, etc. may obtain adhesive strength.

[0024]As the positive active material layer 2 concerning this invention, it is usable as an active material in what etc. has a multiple oxide of transition metals, such as cobalt, manganese, and nickel, charcogen compounds or these conjugated compounds, and various kinds of alloying

elements, for example, without being limited. As the negative electrode active material layer 6, although a carbonaceous material is used preferably, it can concern and use for chemical property in the cell of this invention. What has the granular shape of these active materials is used. It is [particle diameter] usable in a 0.3 to 20-micrometer thing. Especially a 1 to 5-micrometer thing is preferred in respect of the dope of ion, such as a lithium ion at the time of charge and discharge, and dedope efficiency. When particle diameter is too large, unevenness of the surface of the active material layers 2 and 5 in which thin-film-izing of the active material layers 2 and 6 was not easy for, and it the pack density of an active material not only falls, but was formed becomes large, and is not preferred.

[0025]The spacer particle 4 used in order to control the distance (inter electrode distance) between the positive active material layer 2 of an anode and the negative electrode active material layer 6 of a negative electrode is electronic insulation, and it is [spacer particle] chemically usable in a stable material with ionic conduction layer 3 inside. For example, rigid plastic particles, such as ceramics, such as alumina, glass, a divinylbenzene system, and a polymethylmethacrylate system, can be used.

[0026]Although a fiber particle, a spherical particle, scaly particles, etc. can be used for the shape of the spacer particle 4, from a homogeneous viewpoint of inter-electrode distance control nature, its spherical particle which does not have anisotropy in particle shape is preferred.

[0027]About particle size distribution, although the one where the homogeneous viewpoint of inter-electrode distance control to particle size distribution is narrower is desirable, if not less than 80% of all the particles are contained in the 0.3 time thru/or twice as many range of mean particle diameter as this, inter electrode distance is uniformly controllable to a satisfactory grade.

[0028]Since it cannot separate inter-electrode distance certainly about particle diameter if particle diameter is too small, not less than 5 micrometers of mean particle diameter need to be not less than 10 micrometers preferably. Since inter electrode distance will become large more than needed and ion conduction resistance will increase if particle diameter is too large, it has an adverse effect on battery capacity. As for this viewpoint to mean particle diameter, it is preferably preferred that it is 30 micrometers or less 50 micrometers or less.

[0029]As an ion-conductive constituent of non fluidity, the polymer solid electrolyte which dissolved lithium salt, the gel electrolyte which gelled the electrolysis solution by the polymer, etc. can be used for polymers, such as a polyethylene oxide system. From a viewpoint of making ion conduction resistance low, a gel electrolyte is preferred. It is desirable for there to be a method of polymerizing and hardening and a method of swelling the polymer which polymerized beforehand with an electrolysis solution, after mixing a monomer with an electrolysis solution, but to use the former method as a formation method of this gel electrolyte, since control of a presentation can be performed correctly and easily. The spacer particle for controlling inter electrode distance into the fluid which mixed the monomer with the electrolysis solution can be added, and a spacer particle can be easily mixed into the ion-conductive constituent of non fluidity by polymerizing after that.

[0030]Although various things can be used as a monomer for forming a gel electrolyte, an acrylate monomer, a methacrylate monomer, etc. with ethylene oxide chains are preferably used from a

point of the holding power of good polymerization nature and an electrolyte. It is usable in the azobisisobutyronitrile etc. whose polymerization start by heat is attained as a polymerization initiator.

[0031]As an electrolysis solution used in order to form a gel electrolyte, Ethers solvents, such as dimethoxyethane, wood ether, and diethylether, Into independent or mixtures, such as polyethylene oxide of low molecular weight, ethylene carbonate, and propylene carbonate. What dissolved salts, such as LiPF_6 , LiAsF_6 , LiClO_4 , LiBF_4 , LiCF_3SO_3 , $\text{LiC}(\text{CF}_3\text{SO}_2)_3$, and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, can be used.

[0032]Below, as the single electrode layered product shown in drawing 1 is shown below, it is manufactured. The electrode which formed the porous negative electrode active material layer 6 for the electrode in which the porous positive active material layer 1 was formed on the positive pole collector 1, on the negative pole collector 5 again is produced, respectively.

[0033]Production of each above-mentioned electrode is N-methyl pyrrolidone (hereafter). The positive-active-material paste and negative-electrode-active-material paste which mixed and adjusted positive active material and each negative electrode active material to the solution which dissolved binder resin, such as polyvinylidene fluoride, in a solvent, such as abbreviating to NMP, are applied and dried on a positive pole collector and a negative pole collector, respectively, This is rolled and formed in further predetermined thickness.

[0034]It is made to polymerize with heating etc. in the state where made the field of each active material layer counter, piled it up by applying the mixed liquor which mixed the spacer particle of particle size distribution an electrolysis solution, a monomer, and predetermined to the field of one of active material layers of the anode of the produced electrode, and the negative electrode, and it pressurized. [at least] A monomer serves as a gel electrolyte by this polymerization, and it becomes non fluidity, and the problem of liquid leakage can control inter electrode distance with sufficient accuracy by a spacer particle while being lost.

[0035]Although the above-mentioned embodiment showed the example of the monolayer electrode type cell which consists of a single electrode layered product which joined the anode and the negative electrode to the field of the both sides of the ionic conduction layer 3, An anode and a negative electrode can be arranged by turns among two or more ionic conduction layers, two or more electrode layered products may be formed, and cell capacity can be enlarged in proportion to an electrode layered product by having two or more electrode layered products.

[0036]Although the above-mentioned embodiment showed the rechargeable lithium-ion battery, this invention is applicable also to other rechargeable batteries by changing the kind of active material, an electrolytic kind, etc.

[0037]

[Example]Hereafter, working example explains this invention still in detail.

Working example 1.

(Production of an anode) The positive-active-material paste which adjusted LiCo_2O by distributing 87 weight sections, graphite powder 8 weight section, and polyvinylidene fluoride 5 weight section

to NMP, It applied to 200-micrometer-thick thickness with the doctor blade method on 20-micrometer-thick aluminium foil, and this was neglected for 60 minutes in a 60 °C dryer, it changed into the half-dry state, and the anode was produced by rolling in thickness of 120 more micrometers. This anode was cut to 5 cm x 4 cm, and the terminal for current collection (tab) was attached to that end.

[0038](Production of a negative electrode) Mesophase-microbeads carbon (made by Osaka Gas) 95 weight section, The negative-electrode-active-material paste which distributed and produced polyvinylidene fluoride 5 weight section to NMP, It applied to 200-micrometer-thick thickness with the doctor blade method on 12-micrometer-thick copper foil, and this was neglected for 60 minutes in a 60 °C dryer, it changed into the half-dry state, and the negative electrode was produced by rolling in thickness of 120 more micrometers. This negative electrode was cut to 5 cm x 4 cm, and the terminal for current collection (tab) was attached to that end.

[0039](Adjustment of a gel electrolyte mother liquor) As a monomer, 1 functionality monomer (GX-8301: made by Daiichi Pharmaceutical Co., Ltd.) and 2 functionality monomer (PEM-1000: made by Daiichi Pharmaceutical Co., Ltd.) were used.

[0040]As an electrolysis solution, the solution which dissolved LiPF_6 (made in Tokyo Chemicals) in the mixed solution (it is 1:1 at a weight ratio) of ethylene carbonate (made by Kanto Kagaku) and 1 and 2-dimethoxyethane (made by Wako Pure Chem) by the concentration of 1.0 mol/dm^3 was used.

[0041]Azobisisobutyronitrile (made in Tokyo Chemicals) was used as a polymerization initiator.

[0042]As a spacer particle, the product made from a spherical alumina particle (CB-A 20S: Showa Denko K.K.) was used. The mean particle diameter of this spherical alumina particle was 22 micrometers, and was a thing of the distribution included in the range not less than 90% of whose particle is 15-30 micrometers.

[0043]8% of the above-mentioned spacer particle was added by weight to the above-mentioned monomer, the electrolysis solution, and the mixed solution of a polymerization initiator, and the gel electrolyte mother liquor of the composition ratio shown in drawing 2 was produced.

[0044](Production of a cell) The gel electrolyte mother liquor which adjusted [above-mentioned] is applied to the active material layer surface of the above-mentioned anode and each negative electrode, It inserted into the glass plate in the state where it piled up so that both active material layers might furthermore counter, the pressure of 10 g/cm^2 was put on the cell, it heated for 30 minutes at 80 °C, the monomer was polymerized, and the cell was formed.

[0045](Impedance measurement of a cell) The alternating current impedance of the produced cell was measured using the impedance analyzer (HYURETO pucker company make, 4192A). The impedance of this cell was 0.51ohm.

[0046](Short-circuit test) Where the produced cell is inserted monotonously, impedance when the pressure was put on the whole cell was measured. The pressure was increased gradually, when impedance changed rapidly, it judged that the short circuit arose, and the pressure value estimated the ease of carrying out of the short circuit. This cell produced the short circuit by the pressure

more than 0.5 kg/cm^2 .

[0047]The anode and negative electrode which were produced by the same method as comparative example 1. above-mentioned working example 1 are used, Mixture dispersion of the spacer particle shown in working example 1 is carried out to the electrolysis solution which dissolved LiPF_6 (made in Tokyo Chemicals) in the mixed solution (it is 1:1 at a weight ratio) of ethylene carbonate (made by Kanto Kagaku), and 1 and 2-dimethoxyethane (made by Wako Pure Chem) by the concentration of 1.0 mol/dm^3 , After having applied this suspension to the active material layer surface of two electrodes, making the active material layer side of two electrodes counter and piling up, it put between the glass plate by the pressure of 10 g/cm^2 , and the cell was produced.

[0048]This cell is in the state in which between two electrodes carried out the internal short circuit. Charge and discharge were not completed for this internal short circuit.

[0049]Spherical alumina particles (B-A10: made by Showa Denko K.K.) were used for the working example 2. spacer particle, and others produced the cell like above-mentioned working example 1. The mean particle diameter of the spherical glass particles used by this example was 10 micrometers, and was a thing of the distribution included in the range not less than 80% of whose particle is 3-20 micrometers. The composition of the material used in this working example is shown in drawing 2.

[0050]The impedance of this cell is 0.43ohm and produced the short circuit by the pressure more than 0.1 kg/cm^2 .

[0051]Using spherical alumina particles (B-A 05S: made by Showa Denko K.K.) for the comparative example 2. spacer particle, others produced the cell like working example 1. Mean particle diameter was 3 micrometers and this spacer particle was a diameter of a monodisperse particle contained in the range not less than 90% of whose particle is 1-5 micrometers. The composition of the material used by this comparative example is shown in drawing 2.

[0052]This cell is in the state in which between two electrodes carried out the internal short circuit. Charge and discharge were not completed for this internal short circuit.

[0053]Spherical alumina particles (CB-A 30S: made by Showa Denko K.K.) were used for the working example 3. spacer particle, and others produced the cell like above-mentioned working example 1. The mean particle diameter of the spherical alumina particles used by this example was 29 micrometers, and was a thing of the distribution included in the range not less than 90% of whose particle is 20-40 micrometers. The composition of the material used in this working example is shown in drawing 2.

[0054]The impedance of this cell is 0.81ohm and produced the short circuit by the pressure more than 0.6 kg/cm^2 .

[0055]Using the spherical alumina particle (A-13H, Showa Denko K.K. make) with a mean particle

diameter of 55 micrometers for the comparative example 3. spacer particle, others produced the cell like working example 1. The composition of the material used by this comparative example is shown in drawing 2.

[0056]The impedance of this cell is 1.25ohms and produced the short circuit by the pressure more than 0.8 kg/cm^2 .

[0057]Others produced the cell like working example 1 using what mixed the thing (the mean particle diameter of 10 micrometers, 22 micrometers, and 29 micrometers) used for the working example 4. spacer particle in above-mentioned working example 1 thru/or 3 in equivalent amount by the weight ratio. The composition of the material used in this working example is shown in drawing 2.

[0058]The impedance of this cell is 0.75ohm and produced the short circuit by the pressure more than 0.2 kg/cm^2 .

[0059]In this working example, since three kinds of spacer particles were mixed, the particle size distribution of the spacer particle became a little large, therefore control of inter electrode distance became a little inaccurate, it is thought that impedance became a little large and changed into simplistic mist or the state of being easy to happen.

[0060]Using the spacer particle shown in working example 5. above-mentioned working example 1, the quantity of the spacer particle to the mixed solution in a gel electrolyte mother liquor was increased to 16% of the weight, and others produced the cell like working example 1. The composition of the material used in this working example is shown in drawing 2.

[0061]The impedance of this cell is 0.62ohm and produced the short circuit by the pressure more than 0.8 kg/cm^2 .

[0062]Using the spacer particle shown in comparative example 4. above-mentioned working example 1, the quantity of the spacer particle to the mixed solution in a gel electrolyte mother liquor was increased to 50% of the weight, and others produced the cell like working example 1. The composition of the material used by this comparative example is shown in drawing 2.

[0063]The impedance of this cell is 1.07ohms and produced the short circuit by the pressure more than 1.0 kg/cm^2 .

[0064]Using the spacer particle shown in working example 6. above-mentioned working example 1, the quantity of the spacer particle to the mixed solution in a gel electrolyte mother liquor was reduced to 4% of the weight, and others produced the cell like working example 1. The composition of the material used in this working example is shown in drawing 2.

[0065]The impedance of this cell is 0.47ohm and produced the short circuit by the pressure more than 0.2 kg/cm^2 .

[0066]Using the spacer particle shown in comparative example 5. above-mentioned working example 1, the quantity of the spacer particle to the mixed solution in a gel electrolyte mother liquor was reduced to 1.0% of the weight, and others produced the cell like working example 1. The composition of the material used by this comparative example is shown in drawing 2.

[0067] This cell is in the state in which between two electrodes carried out the internal short circuit. Charge and discharge were not completed for this internal short circuit.

[0068] Increasing the quantity of the monomer for forming a working example 7. gel electrolyte, others produced the cell like working example 1. The composition of the material used in this working example is shown in drawing 2.

[0069] The impedance of this cell is 1.3ohms and produced the short circuit by the pressure more than 0.9 kg/cm^2 .

[0070] Reducing the quantity of the monomer for forming a working example 8. gel electrolyte, others produced the cell like working example 1. The composition of the material used in this working example is shown in drawing 2.

[0071] The impedance of this cell is 0.4ohm and produced the short circuit by the pressure more than 0.1 kg/cm^2 .

[0072] Using the inorganic powder (KaowoolBulk1260 middle) of whisker shape for the comparative example 6. spacer particle, others produced the cell like working example 1. The mean fiber diameter was 4 micrometers and the mean fiber length of this spacer particle was 19 micrometers. The composition of the material used by this comparative example is shown in drawing 2.

[0073] The impedance of this cell is 0.68ohm and produced the short circuit by the pressure more than 0.1 kg/cm^2 .

[0074] According to this comparative example, since there was anisotropy in shape at the shape of a fiber with a big spacer particle and dispersion in an interval arose by the position of two electrodes, it is thought that impedance became large.

[0075] Using alumina (AS-20, Showa Denko K.K. make) for the comparative example 7. spacer particle, others produced the cell like working example 1. Although this spacer particle was 20 micrometers in mean particle diameter, that shape was a thing of the roundish infinite form. The composition of the material used by this comparative example is shown in drawing 2.

[0076] The impedance of this cell is 0.64ohm and produced the short circuit by the pressure more than 0.2 kg/cm^2 .

[0077] Since shape is an infinite form, impedance becomes large a little and the spacer particle used for this comparative example is considered that a short circuit also takes place easily.

[0078] The polyolefin system separator film (trade name: Celgard #200, Hoechst A.G. make) currently widely used for the rechargeable lithium-ion battery instead of the comparative example 8. spacer particle is made into the structure put between inter-electrode, Inter-electrode was filled up with the gel electrolyte (a spacer particle is not mixed) used in working example 1, and the cell was formed.

[0079] The impedance of this cell was 1.2ohms and its resistance was high compared with the cell which controlled inter-electrode using the spacer particle. Even if this cell put the pressure of 1.0 kg/cm^2 , it was not short-circuited.

[0080]It is in ** to be shown below from above-mentioned working example and a comparative example. According to working example 1, by using the ionic conduction layer which consists of a polymer containing a spacer particle by which immobilizing was carried out shows that control an inter-electrode distance with sufficient accuracy, without using the separator leading to increase of ion conduction resistance, and the problem of liquid leakage is solved. In the structure which, on the other hand, combined the liquid electrolyte shown in the comparative example 1, and the spacer particle, distance between two electrodes cannot be kept certain. That is, to control the distance between two electrodes by a spacer particle, to combine with the electrolyte of non fluidity is required.

[0081]Like working example 2, when what has a little small particle diameter of a spacer particle is used, the distance between two electrodes becomes small and becomes a tendency which is a little easy to short-circuit as a result, but ion conduction resistance can be decreased. In the comparative example 2, since the particle diameter of a spacer particle was too small, distance between two electrodes could not be maintained, and a short circuit was not able to be prevented. These results show that it is required to be not less than 5 micrometers as mean particle diameter of a spacer particle.

[0082]Like working example 3, when what has a little large particle diameter of a spacer particle is used, it becomes possible for the distance between two electrodes to become large and to prevent a short circuit more effectively as a result, but ion conduction resistance increases a little by one side. In the comparative example 3, since the particle diameter of a spacer particle is too large, it becomes become large too much and high [ion conduction resistance] extremely [the distance between two electrodes]. These results show that it is required to be 50 micrometers or less as mean particle diameter of a spacer particle.

[0083]Working example 4 mixes the spacer particle from which particle diameter differs, and although it is the example which extended particle size distribution, if the particle size distribution of a spacer particle spreads, while the function to hold the distance between two electrodes and to prevent a short circuit will fall, ion conduction resistance also increases. Therefore, although the narrower one of the particle size distribution of a spacer particle is preferred, particle size distribution is understood that it is required to contain not less than 80% of all the particles in the 0.3 time thru/or twice as many range of mean particle diameter as this from the result of above-mentioned working example,

[0084]If quantity of a spacer particle is increased like working example 5, a short circuit can be prevented more effectively and it can be made a reliable cell, but ion conduction resistance increases. Like the comparative example 4, if there is too much quantity of a spacer particle, ion conduction resistance will increase extremely. Like working example 6, when quantity of a spacer particle is lessened, it is in the tendency which becomes a little easy to short-circuit, but ion conduction resistance can be decreased. If there is too little quantity of a spacer particle like the comparative example 5, the result that the short circuit has already arisen in the stage which forms a cell will be brought.

[0085]If the content of the polymer in an ionic conduction layer increases like working example 7, a

short circuit can be prevented more effectively and it can be considered as a reliable cell, but ion conduction resistance increases. If the content of the polymer in an ionic conduction layer decreases like working example 8, although ion conduction resistance falls, a short circuit will produce it by a lower pressure.

[0086][set / the particle diameter of a spacer particle / further / control of ion conduction resistance and inter electrode distance and the quantity of the viewpoint of maintenance to a polymer and the quantity of a spacer particle, and / therefore / appropriately] It becomes possible to be wide range and to control a battery characteristic like the design which gave priority to reliability, and the design which gave priority to battery capacity.

[0087]

[Effect of the Invention]According to the invention concerning Claim 1 and 5, the 1st rechargeable battery, Between the anode which formed the positive active material layer in the positive pole collector, the negative electrode which formed the negative electrode active material layer in the negative pole collector, and the above-mentioned positive active material layer and a negative electrode active material layer, Have an ionic conduction layer which consists of an ion-conductive constituent of the non fluidity containing the spacer particle which controls the distance of this positive active material layer and negative electrode active material layer, and by things. An inter-electrode distance is controlled with sufficient accuracy, without using the separator leading to increase of ion conduction resistance, and the problem of liquid leakage is solved, and it is effective in a highly efficient rechargeable battery being obtained.

[0088]According to the invention concerning Claim 2 and 6, while receiving the ion conduction of an ionic conduction layer by the mean particle diameter of a spacer particle being 5 micrometers - 50 micrometers, control of accurate inter electrode distance can be performed and a short circuit can be effectively controlled by maintenance of the distance.

[0089]According to the invention concerning Claim 3 and 7, by considering particle size distribution of a spacer particle as the distribution by which not less than 80% of all the particles are contained in the 0.3 time thru/or twice as many range of mean particle diameter as this, control of accurate inter electrode distance can be performed and a short circuit can be effectively controlled by maintenance of the distance.

[0090]According to the invention concerning Claim 4 and 8, by making shape of a spacer particle spherical, control of accurate inter electrode distance can be performed and a short circuit can be effectively controlled by maintenance of the distance.

[Translation done.]